Methyl(hydrido)platinum(IV) Complexes That Are Resistant to Reductive Elimination, Including the First (μ-Hydrido)diplatinum(IV) Complex

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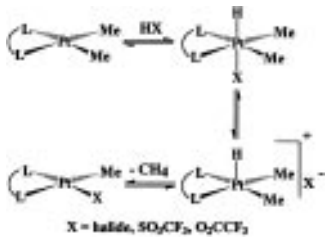
The first examples of methyl(hydrido)platinum(IV) complexes, which are proposed intermediates in the protonolysis of the methylplatinum(II) bond and in methane activation by platinum(II), were reported very recently (Scheme 1).[1] In most cases, these complexes $[PtHXMe_2(LL)]$, where LL is a bidentate nitrogen-donor ligand and X = halide, SO_3CF_3, or O_2CCF_3, are characterized only in solution at low-temperature since, at room temperature, they decompose rapidly. The mechanism of decomposition is proposed to involve dissociation of the ligand X *trans* to the hydride, to form a five-coordinate intermediate which then undergoes easy reductive elimination of methane (Scheme 1).[1b−d]

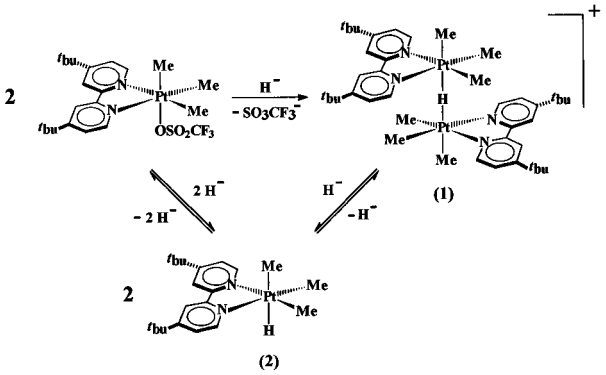
If this mechanism is correct, a complex $[PtHXMe_2(LL)]$ should be stable to reductive elimination of methane if the group X cannot easily undergo dissociation from platinum. This suggested that a complex $[PtHMe_3(LL)]$, in which all ligands are strongly bound, would be stable to reductive elimination. In addition, this complex would have mutually *trans* hydrido and methyl ligands (both with large *trans* effects) and so should, by analogy with the related tetramethylplatinum(IV) complex $[PtMe_4(NN)]$ (NN = 2,2′-bipyridine),[2] give a rich reaction chemistry. Thus the plan was to prepare *fac*-$[PtHMe_3(bu_2bpy)]$ (**2**) (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) from $NaBH_4$ and *fac*-$[PtMe_3(O_3SCF_3)(bu_2bpy)]$, with the O_3SCF_3 ligand acting as a good leaving group (Scheme 2).[3] Although this reaction did occur if a large excess of hydride was present, it proceeded through the unexpected cationic intermediate, $[Pt_2(\mu\text{-}H)Me_6(bu_2bpy)_2]^+$ (**1**), which is the first example of a (μ-hydrido)diplatinum(IV) complex (Scheme 2).

Treatment of *fac*-$[PtMe_3(O_3SCF_3)(bu_2bpy)]$[4] with a stoichiometric amount of $NaBH_4$ in THF solution affords the cationic $[Pt_2(\mu\text{-}H)Me_6(bu_2bpy)_2]^+$ (**1**) which, as the BPh_4^- salt, can be isolated as a yellow powder in 65% yield. Complex **1** is indefinitely stable at room temperature, both as a solid and in solution, which allowed full characterization by ^1H and ^{195}Pt NMR spectroscopies.[5]

Scheme 1



Scheme 2



The ^1H NMR spectrum (300 MHz, CD_2Cl_2) of complex **1** shows the expected three aromatic resonances and one *tert*-butyl resonance due to the two equivalent pyridine moieties of the bu_2bpy ligand. These data rule out the alternative isomer with μ-H *trans* to nitrogen, which would have nonequivalent pyridyl groups. There were two methylplatinum resonances in a 2:1 intensity ratio due to the methylplatinum groups *trans* to bu_2-bpy [δ = 0.47, ^2J(PtH) = 69.6 Hz] and *trans* to hydride [δ = 0.13, ^2J(PtH) = 65.9 Hz], respectively. Both peaks showed a small coupling with the hydrido ligand. The most convincing evidence for a bridging hydrido ligand comes from the low-frequency Pt−H resonance at δ = −11.7 with ^1J(PtH) = 442 Hz (Figure 1). The resonance appears as a 1:8:18:8:1 multiplet due to coupling to ^{195}Pt, thus proving the presence of a $Pt_2(\mu$-H) group.[6] This Pt−H resonance is absent in the ^1H NMR spectrum of $[Pt_2(\mu\text{-}D)Me_6(bu_2bpy)_2]^+$ (**1***), prepared using $NaBD_4$. The $^2H\{^1H\}$ NMR spectrum (30.70 MHz, CH_2Cl_2) of complex **1*** shows only the expected resonance at δ = −11.7 with ^1J(PtD) = 68.4 Hz.[7] The ^1H-coupled ^{195}Pt NMR spectrum (42.92 MHz, THF-d_8) of **1** contains a doublet at δ = −1238 (from $K_2[PtCl_4]$ in D_2O) due to coupling with the bridging hydrido ligand [^1J(PtH) = 440 Hz], thus proving the presence of only a single μ-H ligand. The ^{195}Pt NMR spectrum (CD_2Cl_2) of $[Pt_2(\mu\text{-}D)Me_6(bu_2bpy)_2]^+$ (**1***) shows only a broad singlet at δ = −1240, since the line width ($\Delta\nu^{1/2}$ = *ca.* 160 Hz) is greater than the coupling ^1J(PtD).

Complex **1** is stable in solution in common organic solvents. The presence of a large excess of $NaBH_4$ results in formation of an equilibrium mixture of **1** and 2 equiv of $[PtHMe_3(bu_2$-bpy)] (**2**) (Scheme 2).[8] Under these strongly basic conditions, the complexes decompose slowly with precipitation of metallic platinum, but **2** was readily characterized by ^1H NMR spec-

(1) (a) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (d) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. Personal communication. (e) Canty, A. J. Personal communication.

(2) (a) Hux, J. E.; Puddephatt, R. J. *Inorg. Chim. Acta.* **1985**, *100*, 1. (b) Hux, J. E.; Puddephatt, R. J. *J. Organomet. Chem.* **1988**, *346*, C31.

(3) Note that this route is formally $H^- + Pt(IV) \rightarrow Pt(IV)-H$, in contrast to the route $H^+ + Pt(II) \rightarrow Pt(IV)-H$ used previously.[1]

(4) (a) $[PtMe_3(O_3SCF_3)(bu_2bpy)]$ is conveniently prepared by reaction of $[PtMe_2(bu_2bpy)]$[4b] with MeO_3SCF_3 in ether at room temperature. NMR in $CDCl_3$: $\delta(^1H)$ = 0.66 [s, 3H, ^2J(PtH) = 84 Hz, PtMe *trans* to triflate]; 1.26 [s, 6H, ^2J(PtH) = 67 Hz, PtMe *trans* to bu_2bpy]. (b) Achar, S.; Scott, J. D.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4592. Note that $[PtMe_2(bu_2bpy)]$ is stable in the presence of $NaBH_4$.

(5) Spectroscopic data for **1** as the BPh_4^- salt. NMR (300 MHz) in CD_2Cl_2: $\delta(^1H)$ = 8.21 [d, 4H, $^3J(H^6H^5)$ = 6.3 Hz, ^3J(PtH) = 14.0 Hz, H^6]; 8.09 [d, 4H, $^4J(H^3H^5)$ = 2.0 Hz, H^3]; 7.51 [dd, 4H, $^4J(H^5H^3)$ = 1.9 Hz, $^3J(H^5H^6)$ = 6.2 Hz, H^5]; 1.49 [s, 36H, ^{t}bu]; 0.47 [s, 12H, ^2J(PtH) = 69.6 Hz, ^3J(HH) = *ca.* 1.0 Hz, Pt−Me (*trans* to bu_2bpy)]; 0.13 [s, 6H, ^2J(PtH) = 65.9 Hz, ^3J(HH) = *ca.* 1.0 Hz, Pt−Me (*trans* to H)]; −11.7 [s, 1H, ^1J(PtH) = 442 Hz, Pt−H]. ^{195}Pt NMR (42.92 MHz) in THF-d_8: δ = −1238 [d, ^1J(PtH) = 440 Hz]. We draw **1** with a linear PtHPt bond though $M_2(\mu$-H) groups are usually bent. The degree of bending must be small in this case due to steric effects between substituents on platinum.

(6) (a) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516. (b) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Thompson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299.

(7) γ_H/γ_D = 6.51 ≈ ^1J(PtH)/^1J(PtD) = 6.47.

(8) Spectroscopic data for **2**. NMR (300 MHz) in acetone-d_6: $\delta(^1H)$ = 8.58 [d, 2H, $^3J(H^6H_5)$ = 6.0 Hz, H^6]; 8.51 [d, 2H, $^4J(H^3H^5)$ = 2.0 Hz, H^3]; 7.85 [dd, 2H, $^4J(H^5H^5)$ = 2.0 Hz, $^3J(H^5H^6)$ = 6.0 Hz, H^5]; 1.45 [s, 18H, ^{t}bu]; 0.75 [s, 6H, ^2J(PtH) = 66.0 Hz, Pt−Me (*trans* to bu_2bpy)]; −0.79 [s, 3H, ^2J(PtH) = 43.0 Hz, Pt−Me (*trans* to H)]; −7.0 [s, 1H, ^1J(PtH) = 805 Hz, Pt−H]. Complex **2** is also formed on reaction of **1** with PPh_3 in refluxing acetone and is stable under these conditions.

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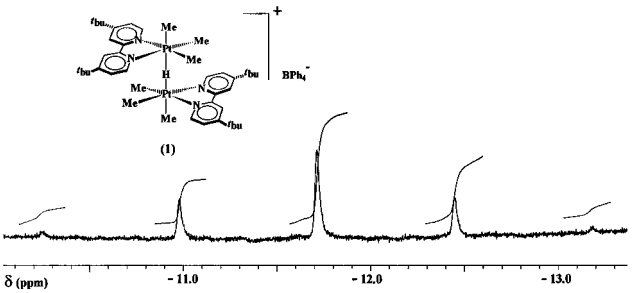

Figure 1. Low-frequency region of the ^{1}H NMR spectrum of **1** in CD_2Cl_2 at 25 °C. The 1:8:18:8:1 intensity ratio in the multiplet due to ^{195}Pt^{1}H coupling is characteristic of a doubly bridging hydride.

troscopy (acetone-d_6) and appears stable to reductive elimination of methane, which would give the stable complex [$PtMe_2$(bu_2bpy)].[4b] Again, the two equivalent bipyridine moieties of the bu_2bpy give rise to three aromatic and one *tert*-butyl resonance. The methylplatinum resonances appear in a 2:1 ratio at δ = 0.75 (*trans* to bu_2bpy) and −0.79 (*trans* to H) with ^2J(PtH) = 66.0 and 43.0 Hz, respectively. Note that the methyl group *trans* to the hydrido ligand has a very low value of ^2J(PtH), which is significantly smaller than that of the methylplatinum ligand *trans* to the bridging hydride in complex **1** [^2J(PtH) = 65.9 Hz] but is similar to that of the mutually *trans* methylplatinum ligands in [$PtMe_4$(bpy)] [^2J(PtH) = 44 Hz].[2] Thus the terminal hydrido ligand in complex **2** has a stronger *trans* influence than the bridging hydride in **1**. The Pt−H ligand resonates at δ = −7.0 with ^1J(PtH) = 805 Hz. This resonance appears as a 1:4:1 multiplet due to coupling to ^{195}Pt, thus proving the presence of a terminal Pt−H group. This coupling constant has approximately twice the magnitude of that found in **1**, which is reasonable since the s-electron density of the hydride is shared between two platinum centers in **1**. Nevertheless, the value of ^1J(PtH) for complex **2** is still significantly smaller than that of [$PtHMe_2X$(bu_2bpy)] (X = Cl, Br, I; ^1J(PtH) = 1589.7, 1630.5, 1655.5, respectively) again illustrating the effect of the *trans* methyl ligand.[1b] The hydride ligand in **2** is *trans* to the strong σ-donor methyl group and so is expected to be much more hydridic in nature than in the latter complexes. It is presumably this hydridic character that leads to reaction of **2** with [$PtMe_3$(O_3SCF_3)(bu_2bpy)] with displacement of triflate to give the stable complex **1**.[9]

In a very recent study, it was shown that the protonolysis of the Pt−C bond by DCl in [$PtMe_2$(tmeda)] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) proceeds through the detectable Pt(IV)-deuteride, [PtD(Cl)Me_2(tmeda)] and that deuterium incorporation into the methylplatinum groups of [PtD(Cl)Me_2-(tmeda)] occurs faster than the reductive elimination of methane.[1c,d] It was proposed that this occurred by dissociation of the chloride ligand to form a five-coordinate complex as in Scheme 1, followed by easy, reversible formation of a Pt(CH_3D) σ-complex.[1d] Since neither [$PtDMe_3$(bu_2bpy)] nor [Pt_2(μ-D)-Me_6(bu_2bpy)$_2$]$^+$ can readily undergo ligand dissociation to form the required five-coordinate intermediate, no isotopic H−D exchange within PtDMe groups would be expected. This prediction was upheld; for example, both the ^{1}H and ^{2}H{^{1}H} NMR spectra of **1*** showed the absence of deuterium incorporation into the MePt groups or of H into the PtD groups, even after several days in solution.

In conclusion, the new methyl(hydrido)platinum(IV) complexes [$PtHMe_3$(bu_2bpy)] (**2**) and [Pt_2(μ-H)Me_6(bu_2bpy)$_2$]$^+$ (**1**), which have no ligand which can easily dissociate, are thermally stable to reductive elimination of methane and to isotopic exchange within Pt(CH_3) groups, thus giving strong support to the theory that both reactions occur within a five-coordinate intermediate [$PtHMe_2$(bu_2bpy)]$^+$.[1] It is the strongly hydridic nature of **2** which leads to formation of the unique (μ-hydrido)-diplatinum(IV) complex **1**. The remarkable thermal stability of **1** is probably due to three factors, namely, the absence of an easily dissociable ligand (see above discussion), the less hydridic nature compared to **2**, and steric protection of the hydride ligand.

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(9) The ligating ability of terminal hydrides in the synthesis of μ-hydrido complexes has been exploited before. Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.